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# NIOBIUM APPLICATION, METALLURGY AND GLOBAL TRENDS IN PRESSURE VESSEL STEELS

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## Abstract

Niobium-containing high strength steel materials have been developed for a variety of pressure vessel applications. Through the application of these Nb-bearing steels in demanding applications, the designer and end user experience improved toughness at low temperature, excellent fatigue resistance and fracture toughness and excellent weldability. These enhancements provide structural engineers the opportunity to further improve the pressure vessel design and performance. The Nb-microalloy alloy designs also result in reduced operational production cost at the steel operation, thereby embracing the value-added attribute Nb provides to both the producer and the end user throughout the supply chain. For example, through the adoption of these Nb-containing structural materials, several design-manufacturing companies are considering improved designs which offer improved manufacturability, lower overall cost and better life cycle performance.

## Introduction

The increasingly severe requirements in customer specifications for heavy plates used in the construction of pressure vessels for petrochemical, chemical and cryogenic reactors are technologically challenging for the steel producers. This situation exists due to constraints within current specifications and restrictions on chemistry. The steel mill must also take into account not only the combination of plate thickness and heat treatment as it strongly influences the mechanical properties of the steel, but also the chemical composition and the metallurgical fabrication parameters and routes. Finally, these steels must be produced cost effectively at high quality levels meeting and/or exceeding customer expectations.

The influence of the heat treatment, plate thickness and the alloying concept of C-Mn steels on the resultant mechanical properties of heavy plates and process metallurgy practices are key considerations in cost effectively producing these pressure vessel steels. The plate producer has to consider all these parameters and their interactions for the plate design. This delicate balance among strength, toughness and weldability demands appropriate process metallurgy parameters that can guarantee an optimal result. It is strongly recommended to involve the steel producer in the plate design during the early stages of the specification development.

## Background Information

In the initial development of pressure vessel steels in North America, Japan, Korea and Europe, grades were initially based on C-Mn alloying design with the main effort to guarantee strength by increasing C and Mn content before the advent of microalloying. Consequently, although yield and tensile strength were increased, the impact toughness and weldability of the plates decreased quite significantly. Then, through the evolution of steel technology, designers began to incorporate various Nb, V, Ti micro-alloying design concepts, thereby achieving properties and a good strength-toughness balance through grain-refinement strengthening and precipitate strengthening. [1]

The pressure vessel plate thicknesses are typically between 10mm to 50mm and are characterized by: 1) high strength and toughness, 2) good cold formability, 3) high fatigue strength, 4) good fracture toughness and 5) favorable weldability. Modern containers, boilers and vessels are divided into many types:

- Thin walled
- Thick walled
- Storage tanks
- Transportable containers
- Propane bottles
- Gas cylinders

There is a growing global pressure vessel market that demands improved performance, fabricability and cost-containment. The pressure vessel plate market is quite diverse with end market segments such as reaction vessels, heat exchanger vessels, storage containers, corrosion-resistant vessels and cylinders of multilayered clad high pressure vessels. The market for LNG and LPG pressure vessels is ever increasing with the growing global demand for natural gas and propane. Boiler plates are used in the manufacture of cylinders and shell covers for low and high pressure boilers. Within some of these product segments, specifications are some of the most stringent for any plate steel. Non-alloyed and/or Nb-bearing microalloyed steels with minimum 460MPa yield strength are applied in many products. More steel producers are beginning to recognize the value of Nb and its grain refinement attribute within the pressure vessel sector.

## Materials and Specification Design Trends

Within the pressure vessel steel sector, it is the end user who demands higher quality steels and is driving the process for improved operational benefits at higher operating temperatures and pressures. Consequently, this condition has led to the construction of higher capacity pressure vessels with thicker walls. Also, more severe requirements in the steel specifications concerning fabrication and in service conditions such as the limitation of the chemical composition and heat treatment conditions of stress relief has challenged the steel designer to find an optimum balance between all influencing mechanical property and welding parameters in order to achieve the best possible steel design at a competitive cost.

The two most popular pressure vessel grades are ASME SA516 or A516 carbon steel and ASME SA387 or A387 alloy steel for ambient and high temperature applications. These two grades represent nearly 75% of the global pressure vessel steel production. The typical carbon manganese SA516-70 is frequently used in pressure vessel construction and may specify microalloy additions on customer request. [2,3] Although, niobium is not specified in this specification, several world class steel producers are adding Nb via the supplementary requirement section of the specification which allows up to 0.02%Nb. Higher Nb or other microalloy levels require customer/supplier agreement. This grade is an example of how to design the microstructure, achieve mechanical properties and find an optimal balance through Nb-microalloying. Similarly, in the SA387, Nb may be added upon customer request. The value of increased Nb levels also allows for lower C plates when ordered as P91 specifying 0.05-0.11%Nb in the product analysis. Table 1 below outlines several pressure vessel grades, properties and associated standards. There are numerous other pressure vessel specifications as well which are too voluminous to outline in this paper.

Table 1. Standards for pressure vessel steels.

| Standard | Production | Grade | | Chemical composition , max (%) | | | | Tensile Test (transverse) | | | Charpy - V-Test (d=16mm) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | Si | Mn | others* | Re min (MPa) | Rm (MPa) | A min (%) | T ( C°) | AV min, J |
| DIN EN 10025-2 | N, AR | S235<br>S275<br>S355 | | .17<br>.21<br>.24 | /<br>/<br>.55 | 1.40<br>1.50<br>1.60 | Cu, Ni, Nb | 235<br>275<br>355 | 360-510<br>410-560<br>470-630 | 26<br>23<br>22 | 20<br>to<br>-20 | 27<br>27<br>27 |
| DIN EN 10028-2 | N | P235<br>P265<br>P285 | | .16<br>.20<br>.20 | .35<br>.40<br>.40 | 1.20<br>1.40<br>1.50 | Cu, Ni, Nb | 235<br>265<br>295 | 360-480<br>410-530<br>460-580 | 24<br>22<br>21 | -20 | 27 |
| DIN EN 10028-3/-5 | N / TM | P275<br>P355<br>P420<br>P460 | | .16 / -<br>.18 /.14<br>- /.16<br>.20 /.16 | .40 / -<br>.50<br>- / .50<br>.60 | 1.50 / -<br>1.70 / 1.60<br>- / 1.70<br>1.70 | Cu, Ni, Nb | 275<br>355<br>420<br>460 | 390-510<br>450-630<br>520-660<br>530-720 | 24<br>22<br>19<br>17 | -20<br>to<br>-50 | 27 |
| ASTM | N | A516 | 60 | .21 | .40 | .90 | Cu, Ni, Nb | 220 | 415-550 | 25 | -51 | 18 |
| | | | 70 | .27 | .40 | 1.2 | Cu, Ni, Nb | 260 | 485-620 | 21 | -46 | 20 |
| | N | A537 | 1 | .24 | .15 / .50 | .70 / 1.35 | Cu, Ni, Nb | 345 | 485-620 | 22 | -62 | 20 |
| | N | A633 | A | .18 | .15 / .51 | 1.00/ 1.35 | Cu, Ni, Nb | 290 | 430-570 | 23 | -60 | 20 |
| | | | C,D | .20 | .15 / .50 | 1.15 / 1.50 | | 345 | 485-620 | 23 | -40 | 27 |
| | | | E | .22 | .15 / .50 | 1.15 / 1.50 | | 415 | 550-690 | 23 | -20 | 41 |
| | N | A662 | A | .14 | .15 / .40 | .90 / 1.35 | Cu, Ni, Nb | 275 | 400-540 | 23 | -60 | 20 |
| | | | B | .19 | .15 / .40 | .85 / 1.50 | | 275 | 440-585 | 23 | -45 | 20 |
| | | | C | .20 | .15 / 50 | 1.00 /1.60 | | 295 | 485-620 | 22 | -32 | 34 |
| | N | A738 | A | .24 | .15 / .50 | 1.50 | Cu, Ni, Nb | 310 | 515-655 | 20 | 30 | 27 |
| | | | B | .20 | .15 / .55 | .90 / 1.50 | | 415 | 585-705 | 20 | | |
| | | | C | .20 | .15 / .50 | 1.50 | | 415 | 550-690 | 22 | | |
| | | | D | .10 | .15 / .50 | 1.00 / 1.60 | | 485 | 585-724 | 20 | | |
| | | | E | .12 | .15 / .50 | 1.10 / 1.60 | | 515 | 620-760 | 20 | | |

* if required

The metallurgist has to adapt the basic steel design and chemistry to both meet the mechanical requirements of material standards like ASME [2,3] or EN10028 [4] and still fall within the chemistry limits of the specification. Certainly, changes to specification chemistries need to be incorporated into the standards in order to better reflect new chemistry guidelines and current process metallurgy practices that improve properties, weldability, fabrication and at lower operational cost for both the steel mill and the fabricator. Through the adoption of increased Nb levels (higher than some currents specs), the opportunity exists to further reduce both C and Mn below current specification minimum levels.

Apart from the mechanical properties at ambient temperature, pressure vessel steels frequently require high temperature demands on the tensile properties approaching 450°C. Niobium-containing plate steels have been shown to increase high temperature properties. [5] Under such conditions, they must also exhibit compatibility with the enamelling/surface coating. Due to the high safety relevance of the pressure vessel, engineering orders are usually subject to the third party inspection for the supply of the heavy plates by different world-wide external third party inspection agencies, like:

- Germanischer Lloyd
- Lloyds Register
- TÜV Nord GmbH
- Det Norske Veritas
- Bureau Veritas.

A pre-condition for the supply of pressure vessel steels is always a third party approval by a certified inspection agency. Quality management system must be followed according to DIN ISO 9001 and proof of the certified manufacturing process is required. Appropriate approvals are given and examined and periodic audits are made for both the product and systems by these third party inspection agencies. The steel mill is then an approved supplier of plates to be used in pressure vessel construction in accordance with the above-mentioned regulations.

The standards limit certain design parameters, but the latest reviews offer new possibilities, e.g. since edition 2007 the ASME standard allows for a higher maximum manganese (Mn) content of 1.50%. The maximum carbon content has to be reduced accordingly. The former editions allowed a maximum Mn content of 1.20%. [6] However, with these increasing Mn levels, segregation and casting issues can affect plate toughness and z-direction properties. The next generation of pressure vessel steels will move toward leaner C and Mn chemistries in order to further improve weldability, fabricability and toughness at both low and high operating temperatures.

## Nb Role in Pressure Vessel Steels

While consumption of energy in the world is rising, there is growing interest in the building of pressure vessels as well in apparatus engineering and equipment construction for the storage of gases or technical liquids. In addition, such tailored steels are used for highly strained components in offshore engineering, in wind power plants and for special pipe steel grades for the manufacture of long-distance pipelines. In all these markets the demand for heavy plates made of tailored steels containing Nb continues to rapidly grow. Here, the positive effect of micro-alloying with Nb is particularly emphasised, which facilitates the ability to meet the most demanding toughness requirements.

The incorporation of the Nb-microalloying approach is the source for opportunities to create innovative rolling strategies and (if necessary) optimised heat treatment conditions to produce a fine grained microstructure in order to meet the highest material property requirements, in particular the toughness and the resistance against brittle failure. Micro-alloying with Nb inhibits grain growth due to the formed carbides and carbonitrides and the critical temperature for the initiation of the grain growth is shifted to higher temperatures. [7]

Since the ASTMA516 limits the allowable Nb, a micro-addition which meets the specification has a significant effect on Charpy V energy. The effect of a 0.015-0.020% Nb addition on the Charpy impact energy from -60° to 0°C in ASTMA516 is compared to non-Nb plates is shown in Figure 1.

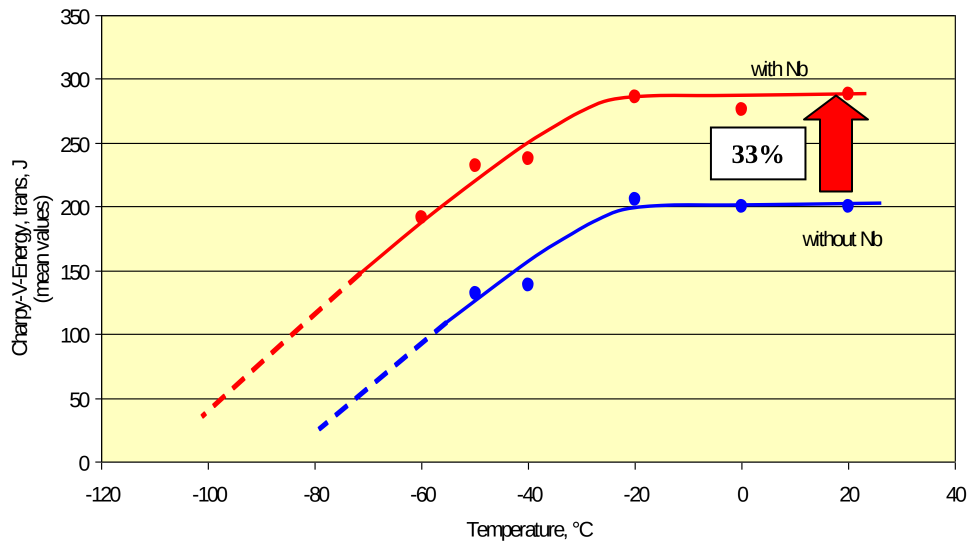


Figure 1. Charpy-V energy (Joules) for P2656GH/ASTMA516Gr.60 [6]

Through the Nb-grain refinement mechanism, at similar C and Mn levels, the upper shelf toughness increases approximately 33% compared to the non-Nb-bearing steel. A case example is described which justifies this MicroNb addition in actual mill operations. This positive shift in the upper shelf has been exhibited is several other pressure vessel grades, but the Nb addition is quite often not published by the producers. They are not required to report the MicroNb level as it is considered a residual element per the specifications, unless otherwise specified. The following case example outlines the steel producer methodology, approach and justification for such a Nb microaddition.

## MicroNiobium Pressure Vessel Case Example

This Nb case example is described for a mill that produces A516Grade 60 plate where the ASTM specification requires minimum 18J Charpy impact energy at -50°C. The internal mill specification for this pressure vessel customer was set at 50J as a safety margin. If less than 50J was tested, these plates will be downgraded to S355 plate (requiring a minimum 27J at -50°C). The mill incorporated an internal spec with this safety margin. When this new spec was initiated, some non-Nb heats fell below the 50J minimum.  Consequently this downgrade to S355 cost the mill several million dollars per year, especially for a high tonnage- high margin critical grade such as A516 Grade 60 and Grade 70.

In normal mill production, it is quite typical to experience some significant Charpy-value scatter and deviation from heat to heat. Many reasons can account for these deviations ranging from segregation issues, high residuals and/or improper reduction schedules (to name a few examples) that lead to inconsistent z-direction impact properties. Thus, the mill decided to make a straight-on comparison. The point here is to make a simple comparison between Nb-containing and non-Nb-containing steels. Figure 2 shows the Charpy scatter plot for plate thicknesses of 8 to 40mm A516 grade.

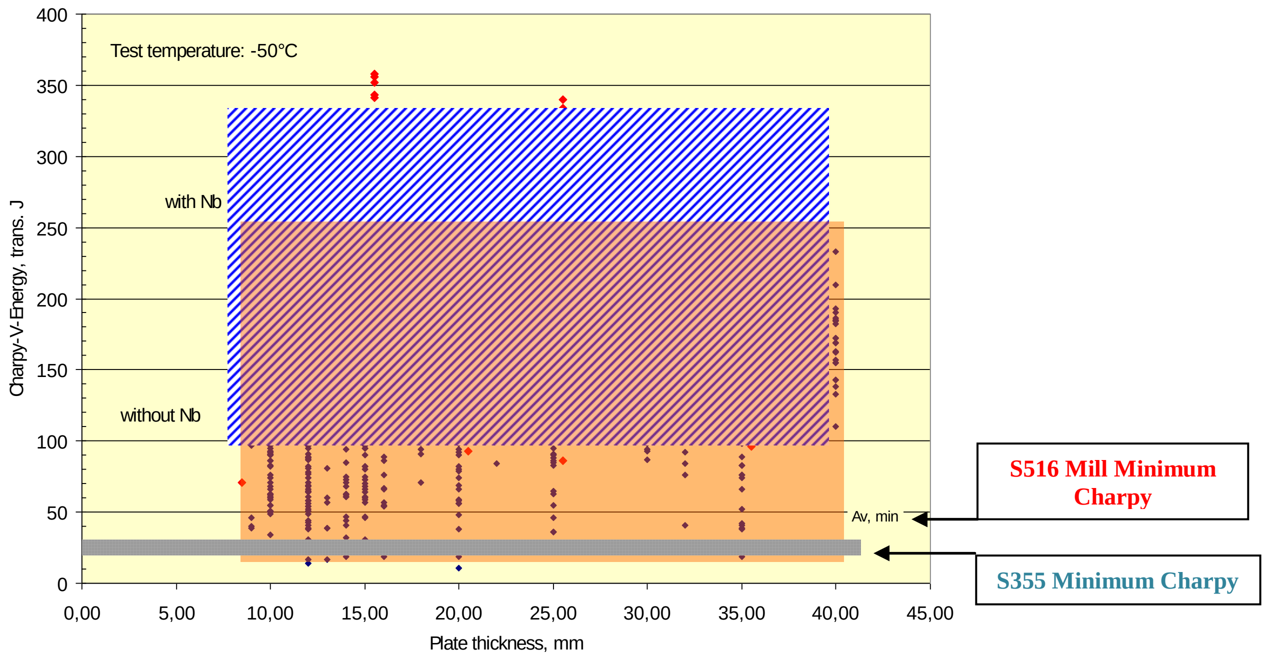


Figure 2. Charpy V energy scatter plot for grade P2656GH/ASTMA516Gr.60 [6]

From Figure 2, one can note the number of heats falling below 50J without Nb compared to the scatter band (in blue) for the Nb-bearing grades. In conclusion, within the combination P265GH/ASTM A516 Grade 60 it is found that the minimum toughness (specified at 27J at -51°C) cannot be achieved with sufficient reliability when testing steels without Nb micro-alloying. Nb is added within the limit values in the range of up to 0.02% as specified in the standards. As a result of the grain refinement, toughness improves and the mean increase of the impact energy at -51°C is approximately 60J. [6]

## Cost Effective Pressure Vessel Process Metallurgy

The economic balance of the process metallurgical practices including the melting, rolling, chemistry development and thermal rolling practices with end user mechanical property demands has become an even bigger challenge for steel developers due to several factors. These factors include escalating raw material and energy prices that result in significant cost benefit challenges for steel producers to meet and/or exceed end user materials engineering demands and expectations at a globally competitive price. The production of value-added microalloyed niobium-bearing steels can be realized through the synergistic development of appropriate steel chemistries along with the proper melting and alloy addition practices, slab and billet reheating furnace practices and specific hot rolling practices to successfully obtain fine grain, homogeneous microstructure. [8]

The past practice of passing on high raw material and operational costs to end users is not sustainable for the long term. The current global competitive environment of the integrated and minimill steel industry necessitates a thorough understanding of the economics of process and physical metallurgy changes made within the ironmaking, steelmaking and rolling processes as well as their effects on product margins, deliveries and overall customer performance.

**Clean Steelmaking Commitment**

The beneficial effects of low sulfur and low phosphorous with strict nitrogen control significantly increase the probability of consistently producing high quality structural steels exhibiting superior fracture toughness and impact strength. The low sulfur and low phosphorous steels improve both the castability and toughness of the steel, minimizing billet, beam, and slab The cross application of the process metallurgy practices applied to other products, such as pipelines, ship plate, beams and heavy machinery, to name a few, can be applied to value added pressure vessel plate. For example, the powerful influence of lower sulfur levels continues to be overlooked when deciding upon a 0.012% or low sulfur practice at 0.005%). Figure 2 illustrates the toughness relationship in a S355 for plate grade at decreasing sulfur levels. Note that for each 50% reduction in sulfur, the Charpy impact strengths are improved at least three to four times.

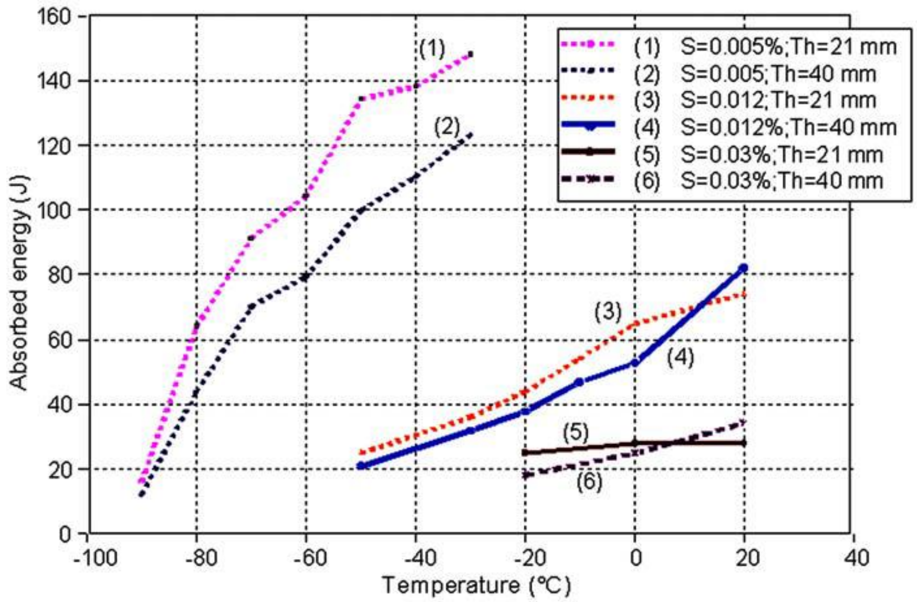


Figure 3. Sulfur effect on Charpy V toughness in transverse direction S355 grade [9]

**Nickel Bearing Pressure Vessel Steels**

The requirement of fracture toughness for pressure vessel and LPG storage tank plates is critical with respect to the crack initiation toughness of the heat-affected zone at the weld and the crack arrestability of the base plate. The combination of lowered carbon content [10] and the addition of nickel [11] improve the crack arrestability of normalized 2.5%Ni steel plate. Since the cost of nickel may be high at times and difficult to predict due to market volatility, the grain refinement developed through thermo-mechanical control with a Nb microalloy addition (0.030%Nb) can replace the more conventional normalized or quench and tempered 2.5%Ni steel plates. This chemistry adjustment will improve the crack initiation toughness of the welded joint and crack arrestability of the base plate.

The 9% Ni steel is increasingly applied in the inner tanks of the double shell for above ground storage tanks for liquefied natural gas. Low silicon 9%Ni plate steels with a small addition of Nb in thicknesses up to 50mm have been successfully applied to 200,000kiloliter LNG storage tanks. The lower Si and C content increase the toughness of the heat affected zone through a reduction in the volume fraction of the martensitic islands. Small additions of Nb from .005 to 0.030% will improve the strength of the base metal as well as the toughness of the heat-affected zone. Table 2 below lists the chemistry of the heats.

Table 2. Chemical compositions of LNG steels [12]

| | **C** | **Si** | **Mn** | **P** | **S** | **Ni** | **Nb** |
|---|---|---|---|---|---|---|---|
| Heat A | 0.05 | 0.25 | 0.60 | 0.003 | 0.001 | 9.0 | - |
| Heat B | 0.06 | 0.08-0.25 | 0.40 | 0.003 | 0.001 | 9.0 | - |
| Heat C | 0.06 | 0.16 | 0.40 | 0.003 | 0.001 | 9.0 | 0.03 |

This low Si-Nb type 9% Ni steel plate of 50mm thickness meets all requirements of JIS G3127 SL9N590 steel plate. The welded joints have sufficient toughness to prevent brittle fracture initiation. Further analysis of the effect of Nb on the toughness of the HAZ reveals improved HAZ properties through the addition of Nb in the range of 0.006 to 0.010%. Both of these applications incorporate the low carbon/clean steel/value-added Nb-microalloying approach. [12]

Pressure vessel steel production in China initiated with development of the 370MPa grade. Subsequently, improvements were made on Charpy v-notch at -20°C, weldability and fabricability with the development of the 15MnNbR grade (570MPa) by WISCO. This grade is successfully applied to LPG and propylene spherical pressure vessels with a maximum volume of 3000 cubic meters. [13]

Research and development has commenced in several regions evaluating the application of Nb in the A553 grade, Type I and II (Pressure Vessel Plates, Alloy Steel, Quenched and Tempered 8 and 8.0 to 9.0 % Nickel) pressure vessel plates. Since the specification allows a range for the Ni, the Nb addition allows for the low side of the Ni range, thereby reducing ferronickel cost at the Melt Shop. For example, in non-Ni grades, within the A514 specification (High-Yield-Strength, Quenched and Tempered Alloy Steel Plate, Suitable for Welding), the grade S allows up to 0.06%Nb, however, the other seven grades do not specify Nb. Similarly, for the A517 (Pressure Vessel Plates, Alloy Steel, High-Strength Quenched and Tempered), the grade S allows up to 0.06%Nb in the heat analysis, while the other seven grades do not. The Nb addition methodology described earlier for the A516 case example will cross apply directly to numerous other pressure vessel specifications.

## Pressure Vessel Plate Steel Technological Grade Development Conclusions

Under current economic conditions, the future pressure vessel grade development trend will focus upon eight areas: 1) grade consolidation, 2) low carbon-low alloy grades, 3) fine grain microstructures through the application of proper finishing temperatures practices and strategic accelerated cooling operational practices, 4) application of cost benefit analysis methodology 5) reduction of C and Mn levels with increased Nb levels, 6) improved z-direction properties through reduced chemical segregation, 7) reduced Charpy impact toughness data scatter and 8) judicious maintenance and capital spending on continuous casting enhancements, mill limitation issues and accelerated cooling upgrades.

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